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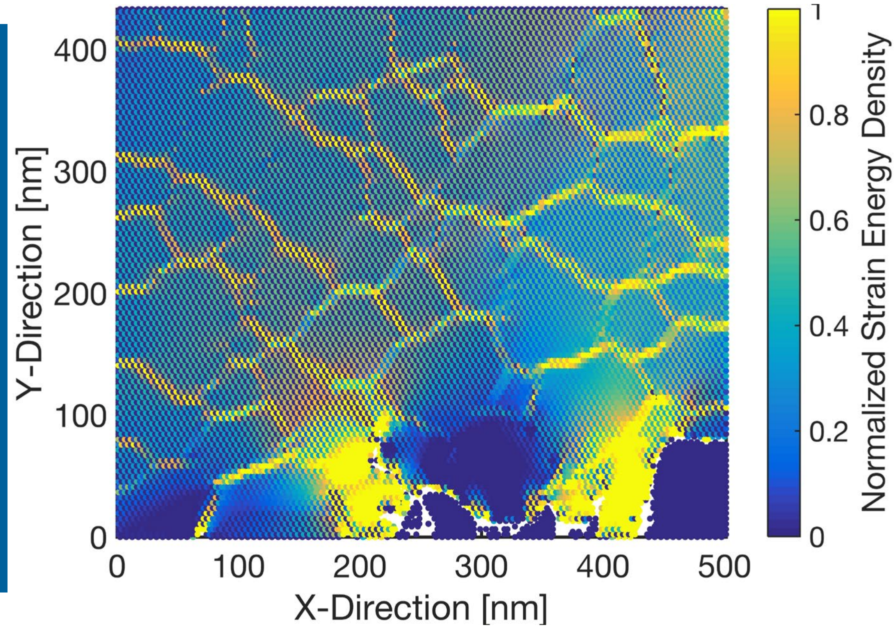
Project ID: **BAT309**

ELECTRODE MATERIALS DESIGN AND FAILURE PREDICTION



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Date: June 13th 2019
Location: Arlington, VA

OVERVIEW

Timeline

- Project start date: October 2016
- Project end date: September 2019
- Percent complete: 90%

Barriers

- Barriers addressed
  - Dendrite growth on lithium metal at different length scales
  - Delamination induced performance decay in cathode/solid-electrolyte interface.

Budget

- $500k/year
  - 0.25 FTE Staff Scientist
  - 1.5 FTE Postdoc
  - 0.5 FTE Graduate Student

Partners

- Kenneth Higa (LBNL)
- Anh Ngo/Larry Curtiss (ANL)
- Nitash Balsara (LBNL)
- Shrayesh Patel (U. of Chicago)
- Neil Dasgupta (U. of Mich.)

RELEVANCE

Objectives:

- Investigate the lithium dendrite growth mechanism from different length scales
  - Large protrusions on the surface of lithium metal, size in the range of 100 nm – 1 micron, lead to dendrite growth
  - Microstructural heterogeneity at the range of 1 nm – 10 nm can cause current focusing and formation of dendritic nucleus

- Elucidation of the degradation mechanism at the solid-state-electrolyte/cathode interface
  - Develop computational models to capture the volume change and stress evolution observed in solid-electrolyte/cathode composite
  - Understand the impact of delamination between solid-electrolyte and cathode on the cell performance decay

MILESTONES

- Investigate impact of grain-interior(GI)/grain-boundary(GB) microstructure on overall dendrite growth observed at SSE/lithium interface. (December, 2018).

Completed

- Analyze effect of delamination at the cathode/SSE interface as a mode of degradation. (March, 2019).

Completed

- Investigate the impact of grain size of the electrolyte on the mechanical degradation occurring at the cathode/SSE interface (June, 2019).

In progress

- *Go/No-Go Decision*: Estimate SOC-dependent impedance at cathode/SSE interface. If not possible, proceed with impedance measured at fixed SOC. (September, 2019).

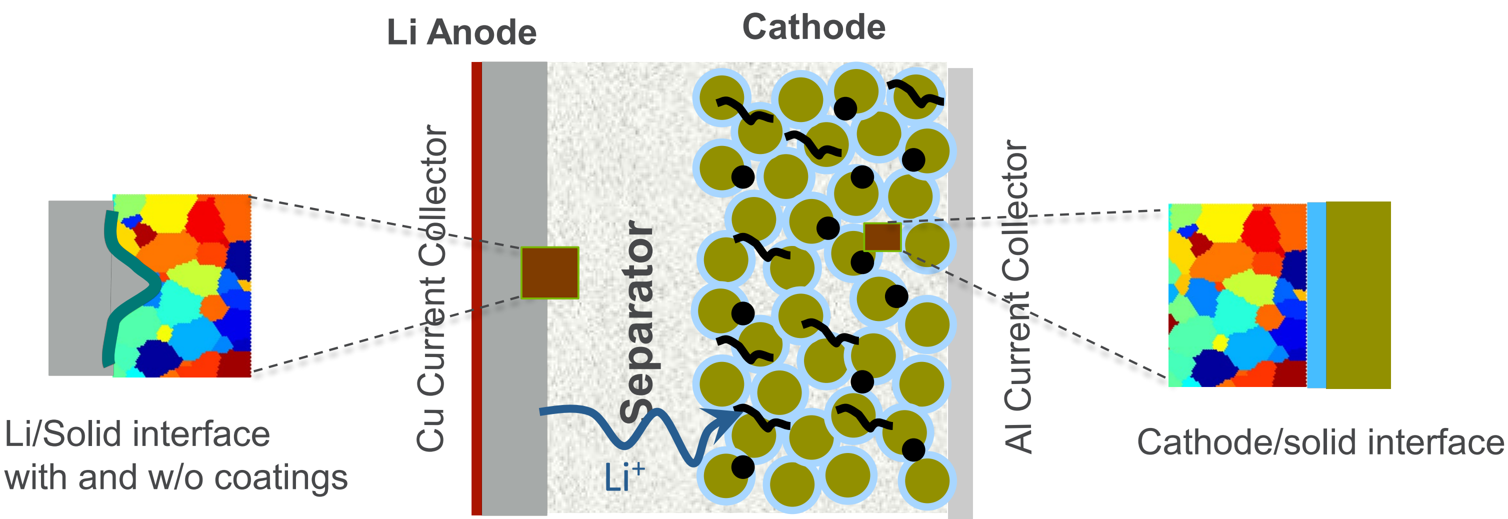
In progress

Sept 2018 | Dec 2018 | March 2019 | June 2019 | Sept 2019

APPROACH

Physics
(Literature: visualization)

Model parameters
(Literature and inhouse: lower length scale theory, experiments)

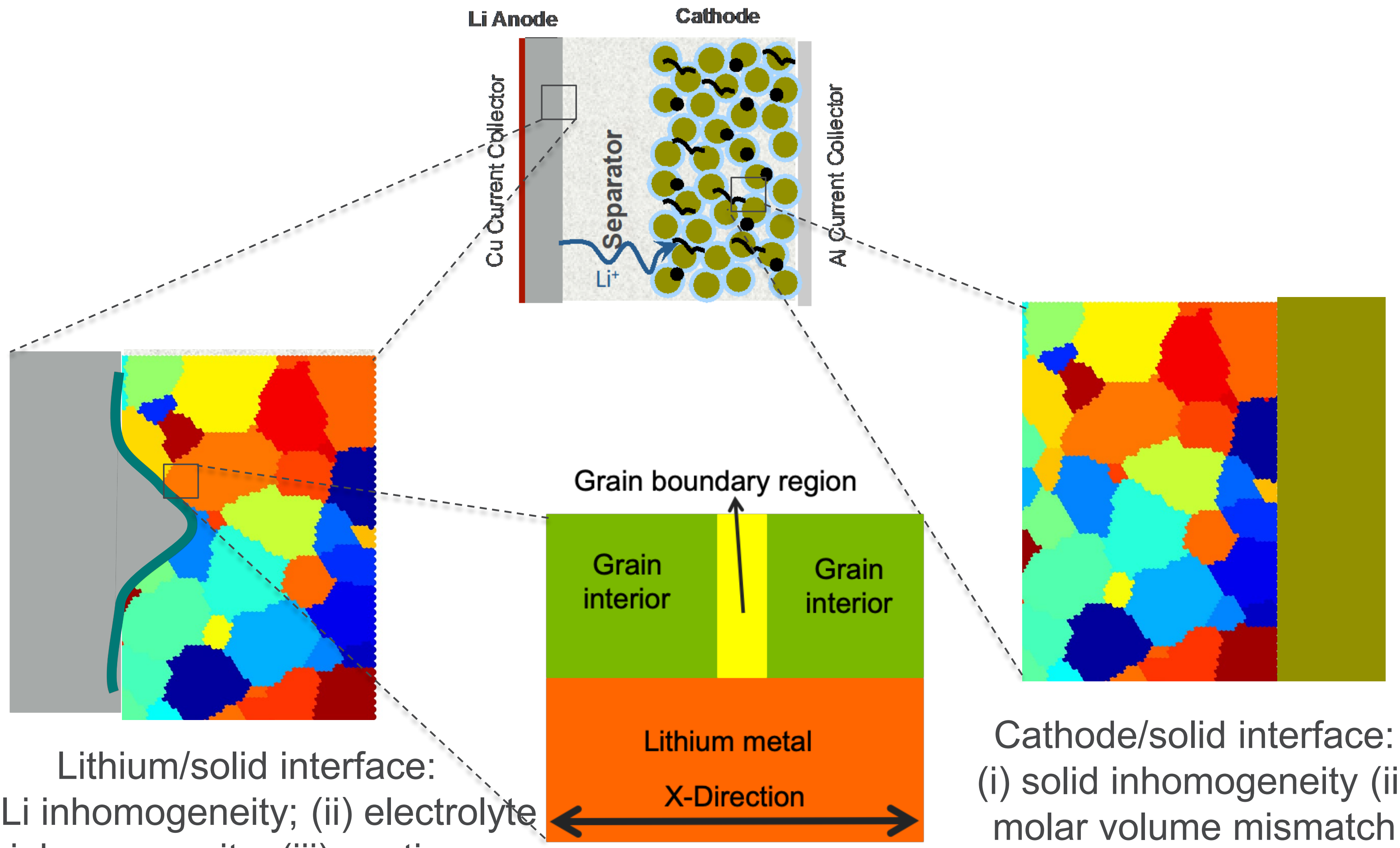


Mathematical modeling at the meso/macro scale
(electrochemistry, transport, mechanics)

Material properties
- Dendrite prevention
- Accommodating volume change

Improve understanding
- Grain boundaries
- Chemo-mechanics at interface

TECHNICAL ACCOMPLISHMENTS: R&D FOCUS AREAS IN THE LAST YEAR



Lithium/solid interface:
(i) Li inhomogeneity; (ii) electrolyte inhomogeneity; (iii) coatings

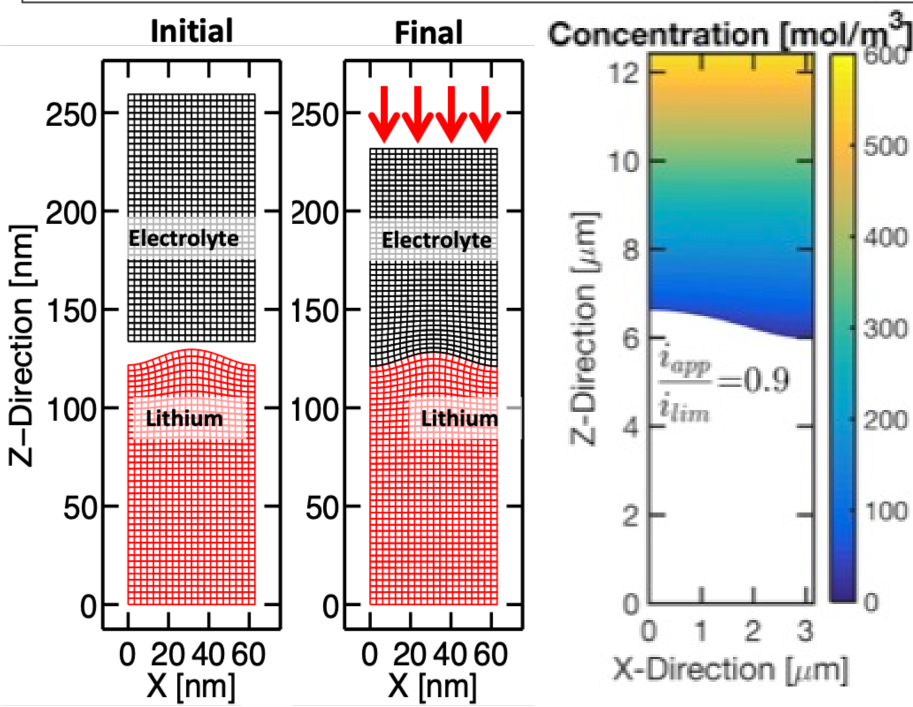
Cathode/solid interface:
(i) solid inhomogeneity (ii) molar volume mismatch

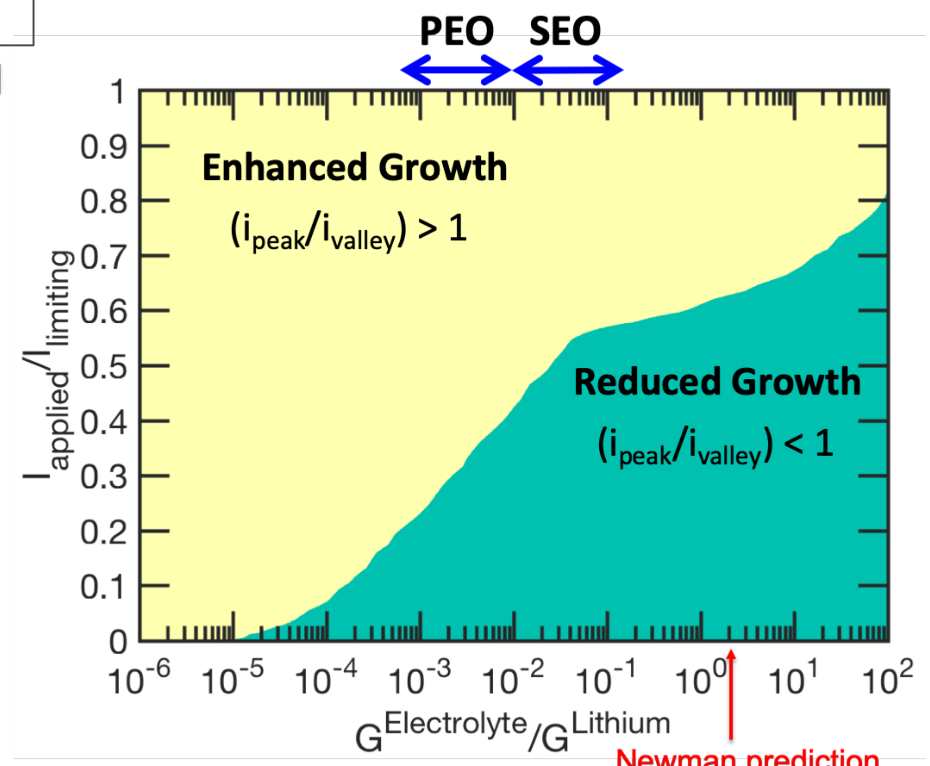
LI INHOMOGENEITIES AND DENDRITE GROWTH

1. *J. Elec. Soc.* , 163, A2216 (2016)
2. *J. Elec. Soc.*, 164, A180 (2017)
3. *Phy. Chem. Chem. Phys.*, 19, 20493 (2017)
4. *J. Elec. Soc.*, 165, A2654 (2018)

$$i_{BV} = Fk_a^{\alpha_c}\left(k_c c_e\right)^{\alpha_a}\left[\exp\left(\frac{F\eta_s}{2RT}\right) - \exp\left(\frac{-F\eta_s}{2RT}\right)\right]\cdot\underbrace{\exp\left(\frac{\Delta\mu_{e^-}}{2RT}\right)}_{\text{Mechanical Stress Factor}}$$

Model include Li and electrolyte plasticity and concentration variations

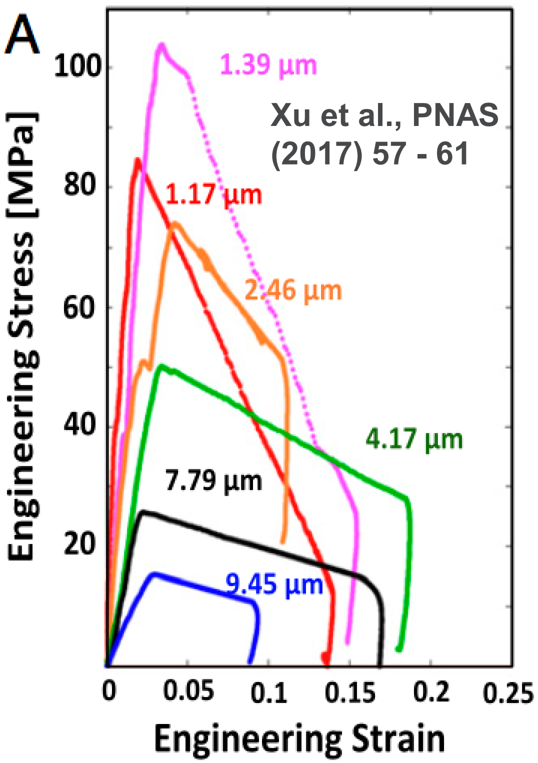


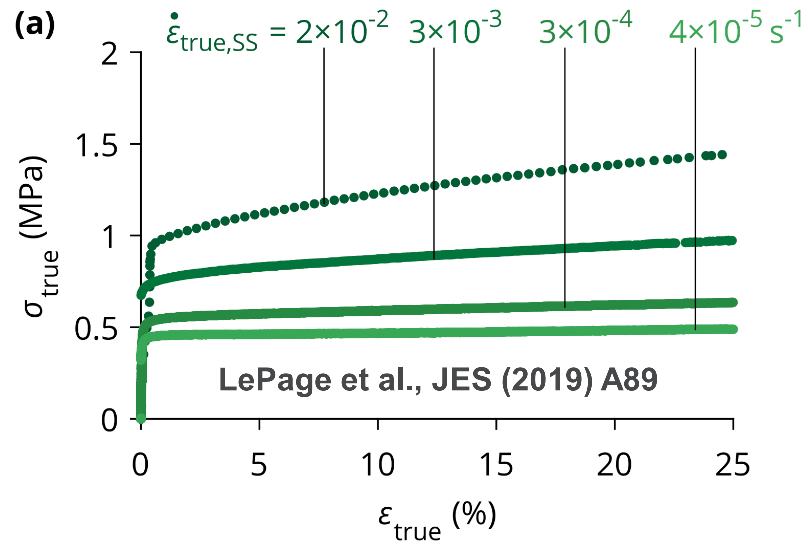


This phase map was obtained assuming lithium yield strength 0.4MPa.

LI YIELD STRENGTH MORE COMPLICATED

Recent experiments have revealed that the yield strength of lithium depends on the rate of deformation, or rate of deposition, as well as size of deposits.





Lithium yield strength increases with increasing rate of deposition

- Campbell et al. Sci. Rep. (2018) 2514

$$\sigma_{0,Li} = 30MPa$$

What are the implications of higher yield strength on dendrite prevention?

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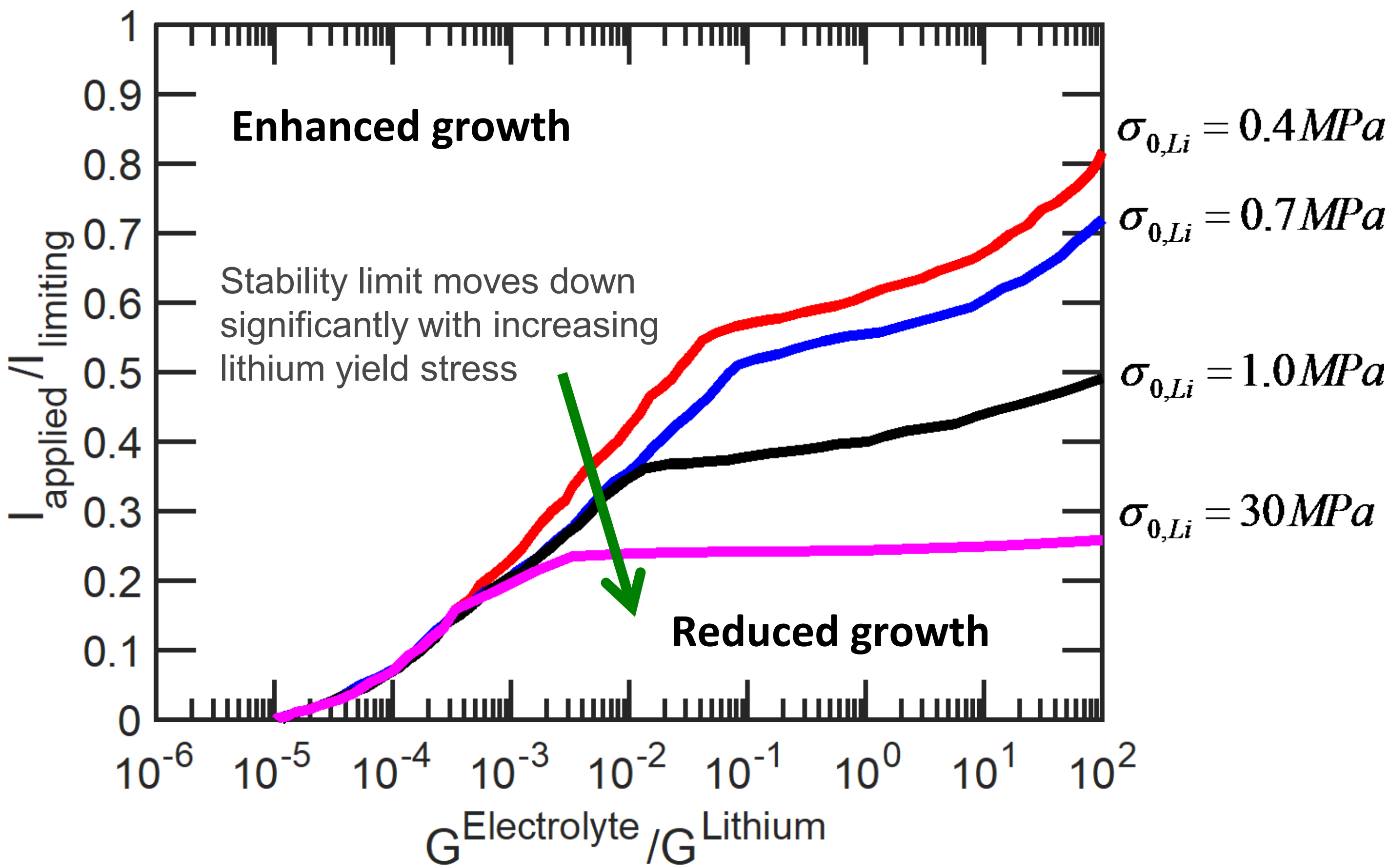
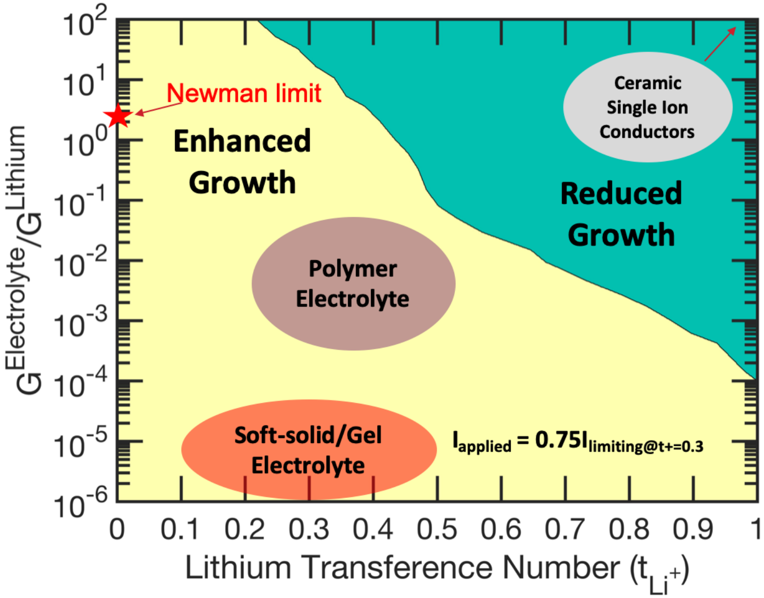
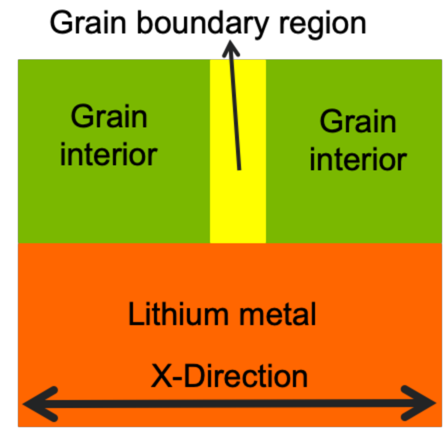
EFFECT OF HIGH LITHIUM YIELD STRENGTH ON STABILITY LIMITS

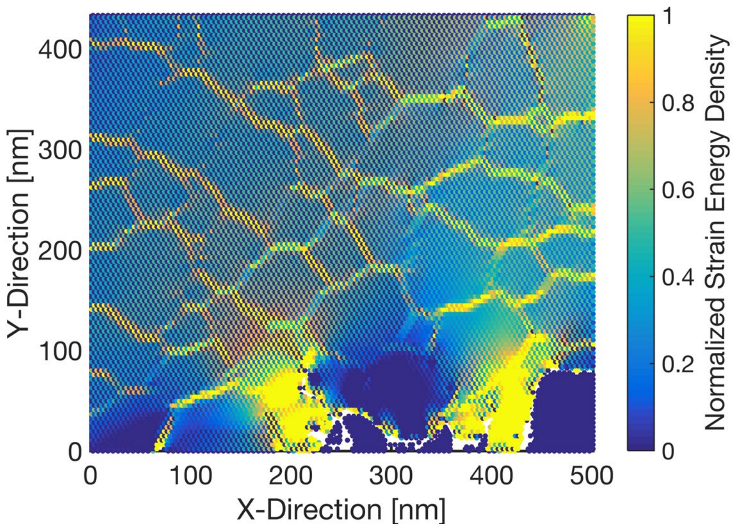


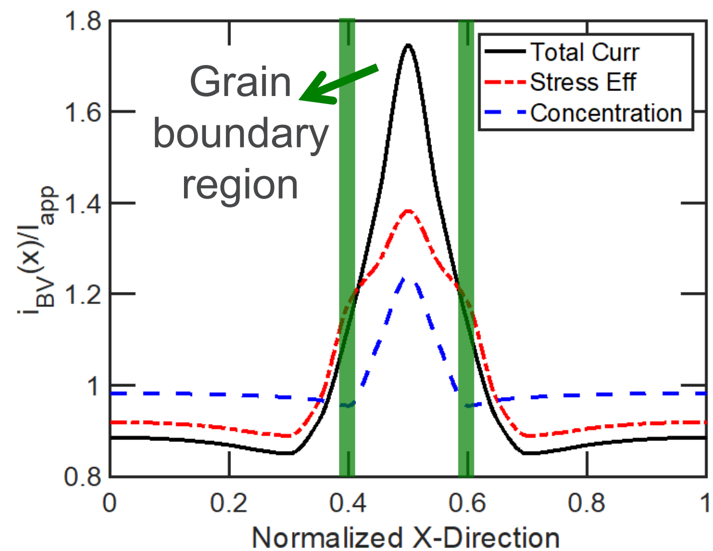
More experimental work is needed to reconcile the behavior of Li

WHY DO DENDRITES GROW IN CERAMICS?







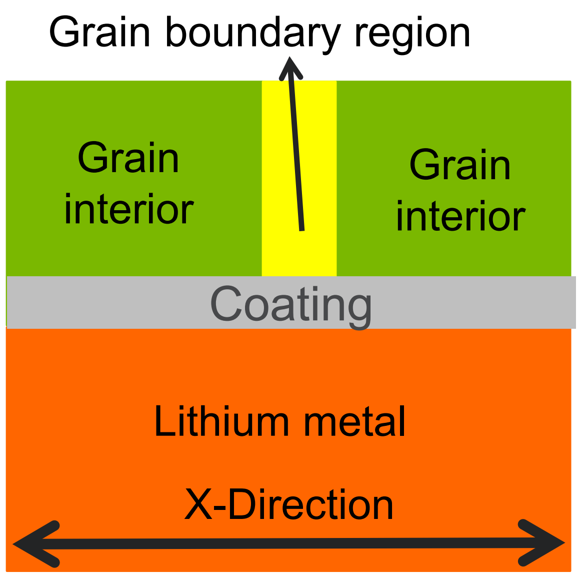


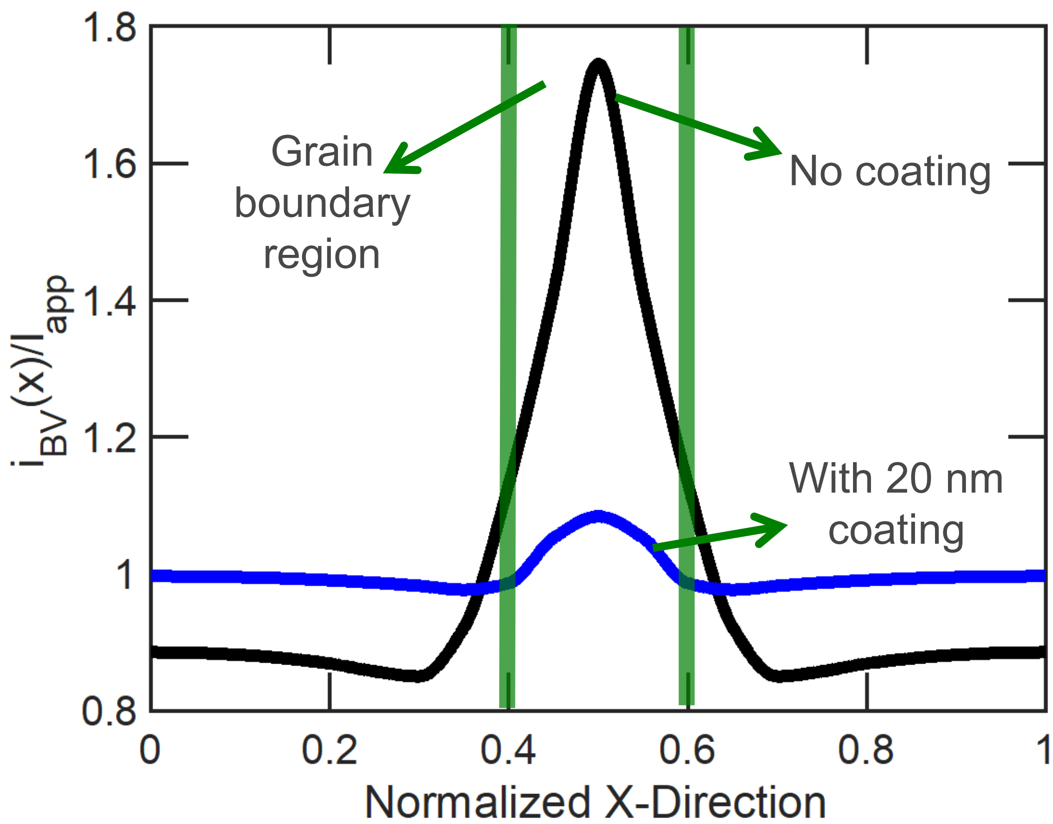
Current focusing at grain boundary. Leads to fracture

(Anh Ngo and Larry Curtiss, BAT424):

1. Elastic modulus: $\mathbf{Y_{GB} = 0.85Y_{GI}}$
2. Conductivity: $\mathbf{\kappa_{GB} = 0.4\kappa_{GI}}$
3. Li concentration: $\mathbf{c_{e,GB} = 1.8c_{e,GI}}$

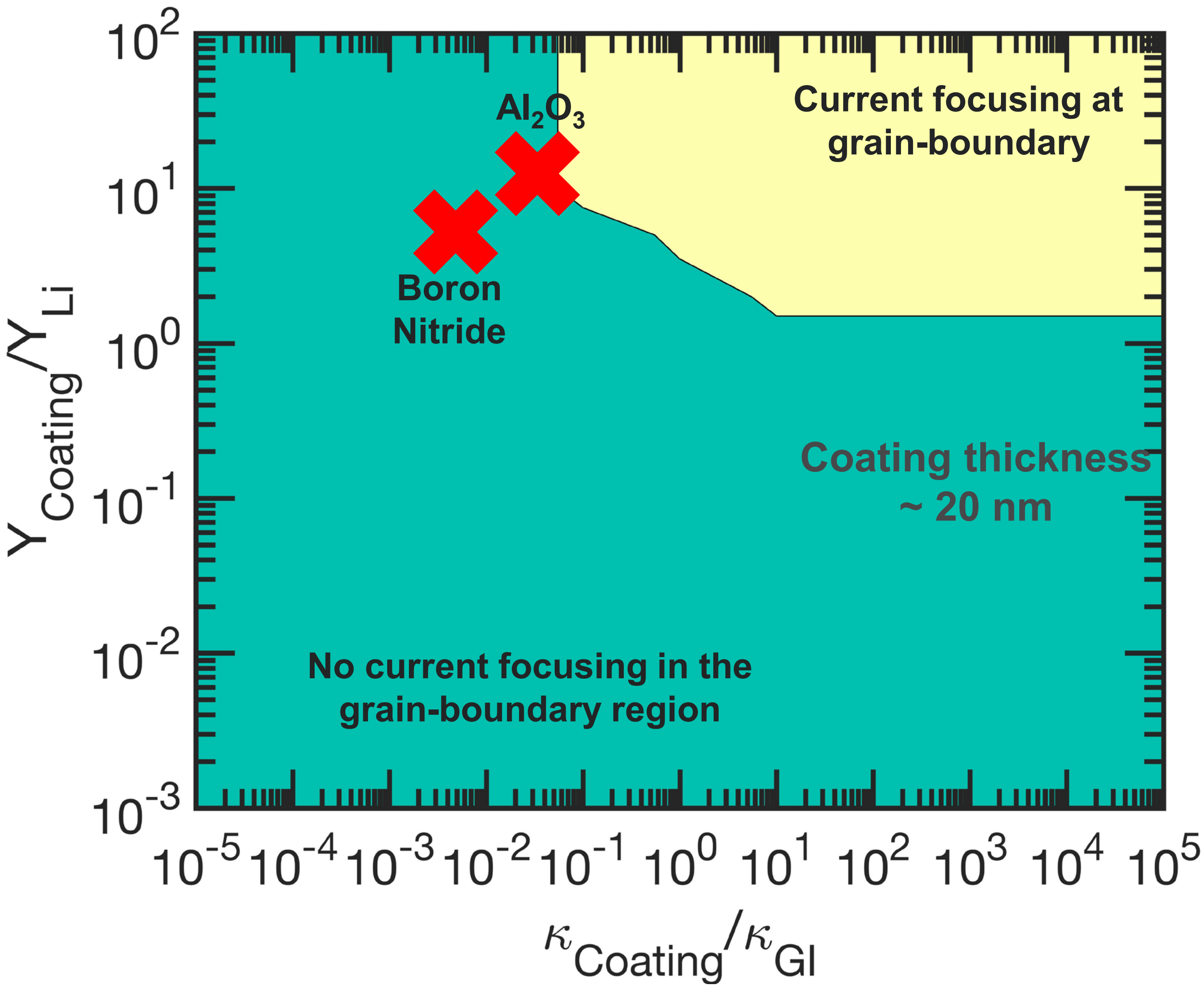
COATINGS PROVIDE A MEANS OF REDUCING THE ELECTROLYTE INHOMOGENEITY





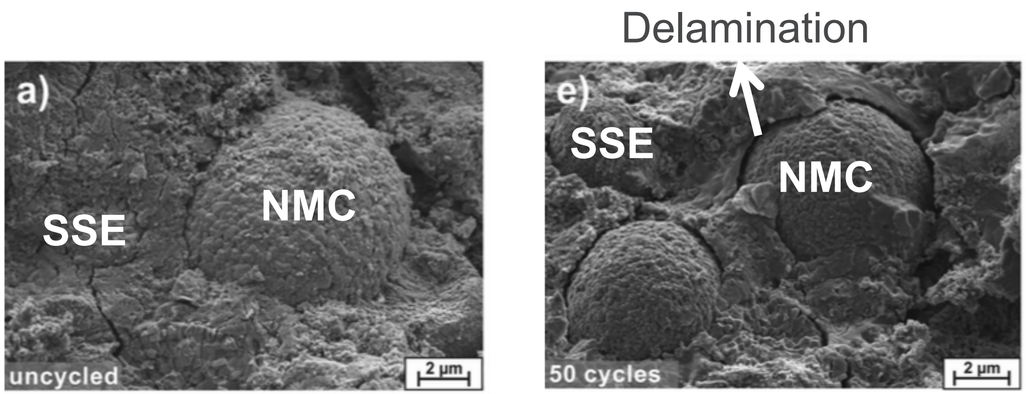
Coatings compensate for inhomogeneities of the ceramic

PREVENTING FOCUSING BY MANIPULATING THE CHARACTERISTICS OF THE COATING



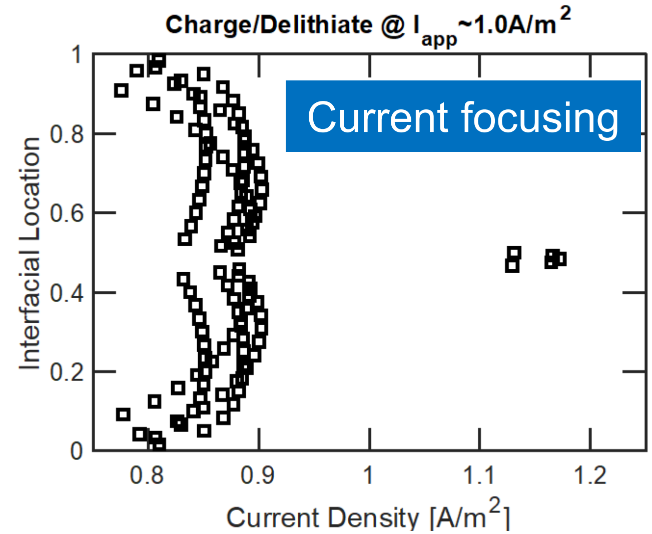
Decreasing elastic modulus and conductivity of the coating material helps to minimize current focusing at the grain boundary region.

MODELING CATHODE-SOLID DELAMINATION

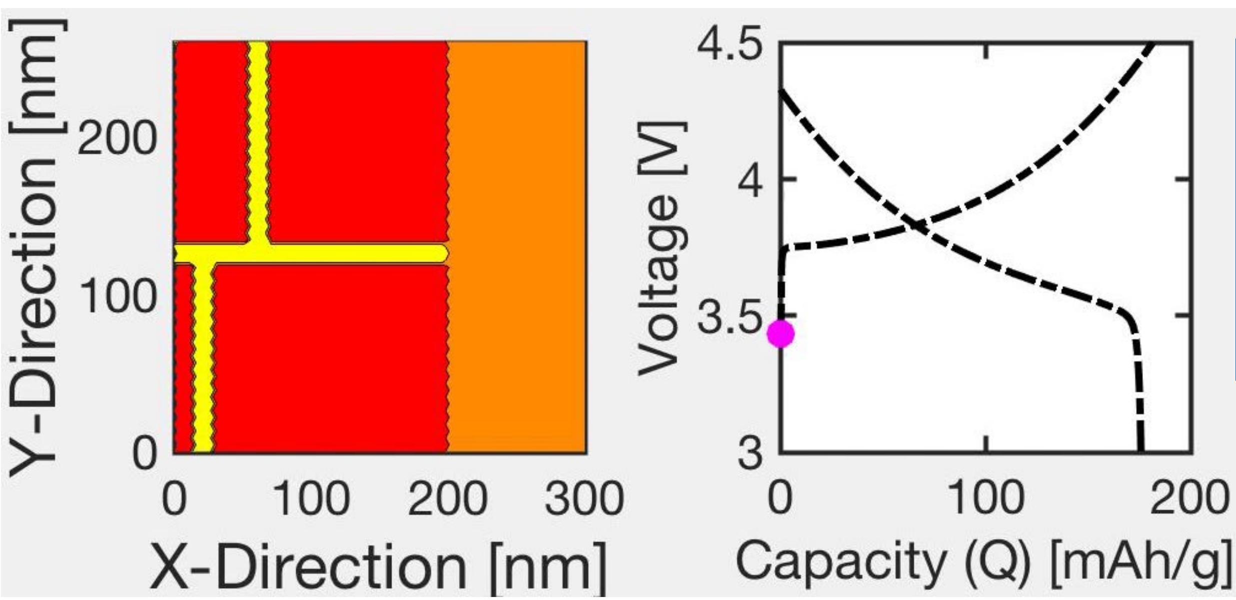


Delamination between the cathode and SSE occurred during repeated cycling.

Koerver et al., Chem. Mater. (2017) 5574



Fracture energy: **J_{LLZO} ~ 10 J/m^2** (Wolfenstine et al. Mater. Lett. (2013) 117 – 120)

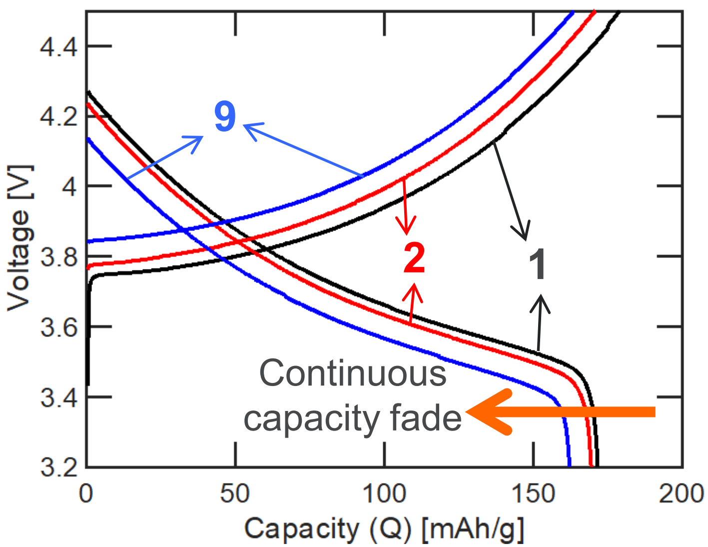


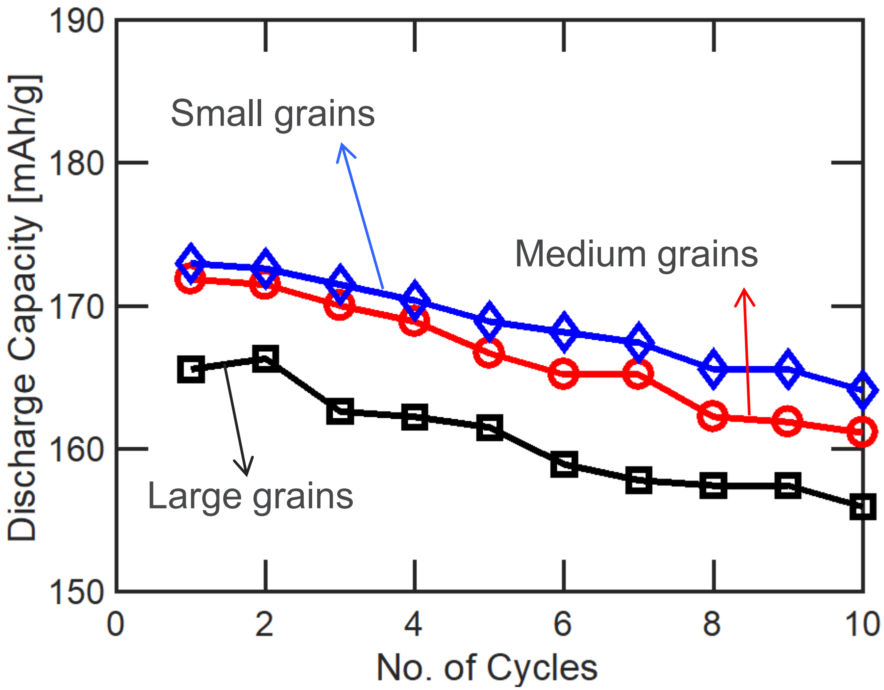
Delamination depends on grain structure of the solid and the cathode molar volume change

EFFECT OF CYCLE NUMBER ON DEGRADATION OF CELL PERFORMANCE

I_{app} ~ 1A/m^2

Large grains





We are now examining the impact of adding buffer layers to minimize delamination

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RESPONSE TO PREVIOUS YEAR REVIEWER'S COMMENTS

This project was not reviewed last year

COLLABORATION AND COORDINATION

- Kenneth Higa (LBNL)
- Nitash Balsara (LBNL)
- Neil Dasgupta (U. of Michigan)
- Shrayesh Patel (U. of Chicago)
- Ang Ngo/Larry Curtiss (ANL): BAT424

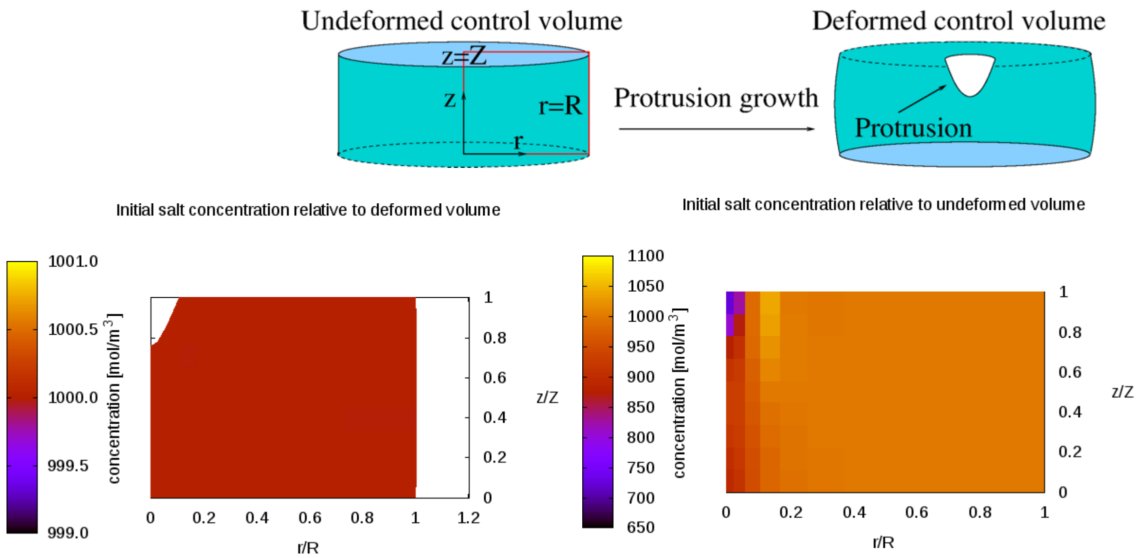
- DOE User Facility
  - Advanced Light Source (ALS), located in LBNL
  - Advanced Photon Source (APS), located in ANL

REMAINING CHALLENGES AND BARRIERS

1. While the model predicts regions where dendrites growth is suppressed, dendrites still grow, but slowly. Can we develop a model that can predict shorting?
2. Can we reconcile the differing values of Li yield strength?
3. Can cathode coatings provide a means of promoting adhesion between the two solids?

PROPOSED FUTURE WORK

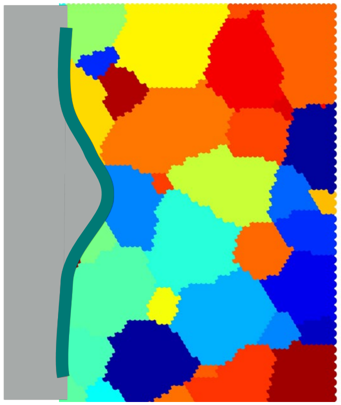
1. Develop a dendrite growth model, accounting for change in shape due to current distribution and mechanics (with LBNL)



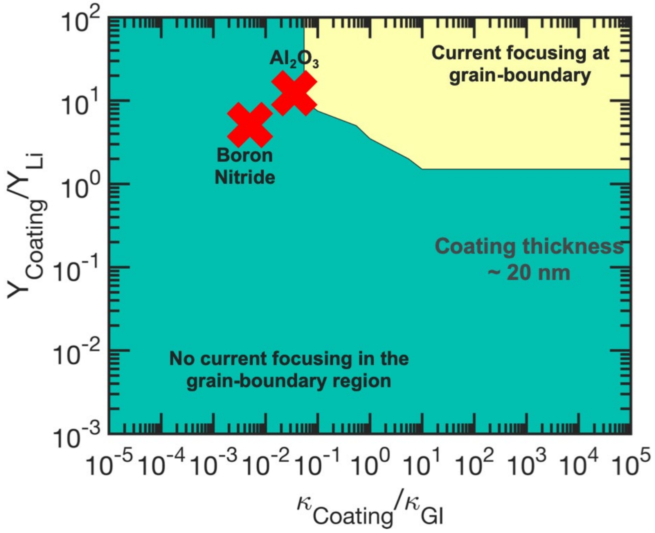
2. Can we incorporate the properties of the actual SEI/CEI layer that forms at the Li/solid and cathode/solid interface? (with ANL)

3. Can we provide guidance for materials properties for a solid state batteries with *experimental validation*? (with ANL)

SUMMARY



1. Developed mathematical models that can predict dendrite growth.



2. Model provides guidance for material properties needed to prevent dendrites

3. Model for cathode/solid shows the drivers for delamination